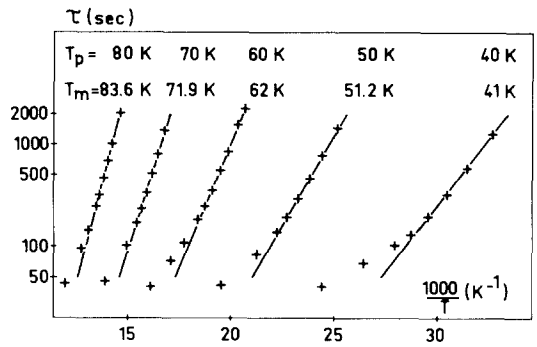

FIG. 3. BFG plots in the low-temperature region. T_m is the temperature maximum for each isolated peak.

We observe in Table I two sets of values for τ_0 with a jump by two orders of magnitude. The values of about 10^{-9} and 10^{-7} s, respectively, are obtained as the polarization window falls into the γ_1 or γ_2 temperature region. As the activation energy varies smoothly we can deduce that the γ_1 and γ_2 processes have their relaxation time mainly distributed in activation energy, with preexponential factors of about 10^{-9} and 10^{-7}, respectively.

In conclusion, we have designed a gas-exchange cryostat to record total TSD spectra or thermal sampling responses for any polymer film dielectrically active in the low-temperature region (77–5 K). This technique was applied here to low-density polyethylene, and it was demonstrated that the γ relaxation of this material is composed of two main processes distributed in activation energy.

The author is indebted to ATO-Chimie for providing the samples.

TABLE I. Numerical values for activation energy E and preexponential factor τ_0 of the relaxation time for each thermal sampling isolated process.

T_p (K)	130	120	80	70	60	50	40
E (eV)	0.25	0.24	0.15	0.13	0.10	0.07	0.05
τ_0 (s)	3.0×10^{-9}	4.1×10^{-9}	7.4×10^{-9}	5.8×10^{-9}	1.3×10^{-7}	7.4×10^{-7}	3.1×10^{-6}

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Reversible phase transformation in the Pd_2Si-PdSi thin-film system

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The thermal stability of thin PdSi films has been studied at temperatures ranging between 300 and 700 °C. The PdSi, when in contact with crystalline Si, transforms into Pd_2Si and Si at temperatures of 500–700 °C, a process contrary to the equilibrium-phase diagram. The rate of transformation was found to depend on the structure and orientation of the Si. Upon heating above 750 °C, Pd_2Si transforms back to PdSi. However, PdSi is stable against annealing when in contact with Pd_2Si or an inert substrate SiO_2. We propose that the decomposition of PdSi into Pd_2Si and Si in the presence of crystalline Si is due to a lower interface energy of the Pd_2Si-Si interface compared to that of the PdSi-Si interface.

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The reaction between a thin Pd film and a crystalline Si substrate is characterized by the formation of a planar Pd_2Si layer at temperatures of $\lesssim 200$ °C and the transformation of this silicide into PdSi at temperatures above 700 °C.[1,2] In contrast to the well-defined layered structure of Pd_2Si, the PdSi grown thermally on Si exhibits a nonuniform structure containing isolated PdSi islands and Si.[2,3] This nonuniform structure blurs the meaning of electrical measurements such as resistivity and the Schottky barrier height of this silicide phase.

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Recently, transient annealing with laser or electron beams has been applied to react thin Pd films on Si substrates. Silicide layers with structures not attainable by normal thermal treatment can be obtained. For example, uniform PdSi silicides have been formed by annealing a Pd film on Si with a scanning cw laser[4] or a scanning electron beam[5] at proper power levels. The effective annealing time is of the order of milliseconds. However, if a pulsed layer of 30–100 nsec duration is used, a layer containing mixed Pd silicides (PdSi, Pd_2Si, Pd_3Si, etc.) is obtained[6] as a result of melting, interdiffusion, and solidification of the Pd film and part of the Si substrate. The thermal stability of this multiphase layer has been studied by subsequent furnace annealing between 300 and 700 °C.[7] It was found that the multiphase layer transforms into a single-phase layer containing only Pd_2Si. This result indicates that the PdSi phase originally present in the mixture decomposes into Pd_2Si and Si during annealing, although the equilibrium-phase diagram shows that PdSi should be stable in contact with Si at temperatures below 850 °C.[8] The result also seems contrary to what we have recently reported on the ion-induced formation of the PdSi[9]: Once formation of PdSi is initiated near the Pd_2Si-Si interface by ion bombardment, growth of PdSi at the expense of Pd_2Si can proceed after postannealing at 350–400 °C, resulting in the formation of a uniform PdSi layer on Si. In the present work, a systematic study of thermal stability of thin PdSi films formed by laser annealing, ion-beam mixing as well as thermal annealing was carried out in an attempt to clarify this contradiction.

To obtain samples with a symmetrical configuration of Si|PdSi|Si on SiO_2 substrates a sandwich structure Si|Pd_2Si|Si was first made by sequential *e*-gun deposition of Si (~1000 Å), Pd (300 Å), and Si (1000 Å) films onto SiO_2 substrates and followed by an annealing at 250 °C for 30 min to form Pd_2Si. The evaporation was performed in an oil-free vacuum system with pressure less than 3×10^{-7} Torr during the deposition. Implantation with 300 keV 1×10^{15} Si ions/cm^2 through the embedded Pd_2Si layer was then carried out to initiate formation of PdSi near the two Pd_2Si-Si interfaces.[9] Postannealing of implanted samples at 400 °C for 30 min resulted in the formation of Si|PdSi|Si structure. PdSi films without Si overlayer have also been prepared by scanning the cw laser annealing and thermal annealing of Pd films on crystal Si substrates as well as the ion-beam mixing techniques. The details of sample preparation procedures have been previously reported.[4,9] Thermal treatments of those PdSi layers were performed in a quartz tube vacuum furnace with a pressure less than 1×10^{-6} Torr. The composition and structure of the annealed layers were analyzed by MeV $^4He^+$ ion backscattering and glancing incidence x-ray diffraction (Read camera).

TABLE I. Results of x-ray analysis of Si|PdSi|Si structure before and after annealing between 400 and 700 °C.

Annealing conditions	Intensity of x-ray diffraction for polycrystalline PdSi	Pd_2Si	Si
Before annealing	Strong	Nil	Nil
400 °C, 1 h.	Strong	Nil	Nil
500 °C, 1 h.	Strong	Nil	Weak
600 °C, 1 h.	Medium	Medium	Medium
700 °C, 1 h.	Weak	Strong	Strong
700 °C, 10 h.	Nil	Very strong	Strong

The purpose of preparing samples with symmetric Si|PdSi|Si structure is to reduce possible effects of the ambient on the PdSi during thermal treatments. Table I shows the results observed by x-ray diffraction analysis for the Si|PdSi|Si samples under various annealing conditions. The as-deposited Si layers were amorphous, and they remained mostly amorphous during the formation of PdSi upon annealing at 400 °C for 30 min. After successive heat treatments with increasing temperature, the intensity of PdSi lines disappears gradually while those of the Pd_2Si phase and of the polycrystalline Si emerge. After annealing at 700 °C for 10 h, only Pd_2Si and Si lines are present. Backscattering analysis revealed significant intermixing between PdSi and Si. Annealing thus results in the formation of a mixture containing Pd_2Si and polycrystalline Si at the final stage (Table I). A similar transformation of PdSi into Pd_2Si and Si was observed for samples without a Si overlayer, i.e., for samples of configuration SiO_2|Si|PdSi. This indicates that the interaction between PdSi and ambient (or the PdSi-vacuum interface) is not a significant factor in the decomposition of PdSi. The experiments described in the following sections were performed on samples without a Si overlayer.

To examine the stability of the PdSi phase alone, we have performed experiments on a PdSi layer formed on an inert substrate of SiO_2. Samples were prepared from two Pd and Si films whose thicknesses were adjusted to correspond to a composition of PdSi. The PdSi was obtained by combining ion-beam mixing and thermal annealing as described previously. Since precise control of thickness is necessary to achieve a single homogeneous phase, several evaporations were carried out and a pure PdSi phase has been obtained. Upon postannealing at 700 °C for 5 h, we found that the PdSi phase remained stable as indicated by x-ray diffraction measurements. However, if the initial composition deviates from PdSi, the stability of PdSi depends on the excess phase. For a Pd-rich layer, the sample was found to contain PdSi with a small amount of Pd_2Si. This two-phase layer is stable and no phase transformation is observed upon annealing up to 700 °C for 5 h. For a Si-rich layer, the sample contained PdSi and excess Si. However, the presence of Pd_2Si is detected upon annealing, and most PdSi transforms into Pd_2Si and Si after annealing at 700 °C for 5 h. This result is similar to that described in the previous paragraph and suggests that PdSi decomposes into Pd_2Si and Si only in the presence of excess Si.

This observation draws attention to the role of the PdSi-Si interface on the stability of PdSi. We therefore prepared PdSi films on single-crystal Si substrates of ⟨100⟩ and ⟨111⟩ orientations. The PdSi films were produced by scanning cw laser annealing of samples with an initial structure, Si⟨xtal⟩/1000 Å Pd/200 Å Si.[4] The thin Si overlayer serves as an antireflection coating for the Pd films. The PdSi films so obtained were quite uniform as indicated by backscatter-

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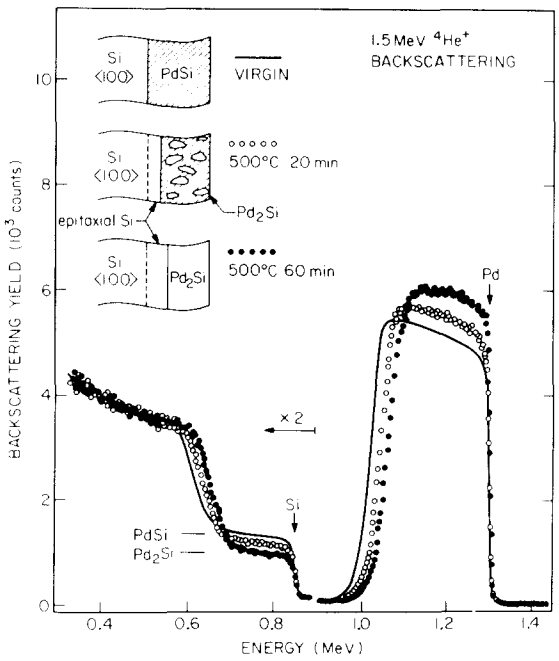

FIG. 1. Ion backscattering spectra which show the decomposition of PdSi into Pd_2Si and Si. The PdSi/Si ⟨100⟩ sample was prepared by a cw argon laser scanning of Si|Pd|Si ⟨100⟩ (see text). The excess Si grows epitaxially onto the Si ⟨100⟩ substrates.

ing measurements. Table II shows the results of x-ray diffraction analysis of these films after thermal annealing between 500 and 700 °C. A decomposition of PdSi is observed on both substrate orientations, but the transformation is clearly faster on ⟨100⟩ than on ⟨111⟩. In contrast to the results summarized in Table I, no polycrystalline Si diffraction lines were detected, which suggests that the excess Si might grow epitaxially onto the single-crystal Si substrate. Such epitaxial growth was confirmed by backscattering and channeling measurements. Figure 1 shows the backscattering spectra of a laser-induced PdSi film on Si⟨100⟩ after thermal annealing at 500 °C for 20 and 60 min. The thickness of the Pd-Si layer decreases during the annealing (20 min), yet the composition remains quite uniform. The insets schematically represent the sample configuration deduced from backscattering, channeling, and x-ray diffraction measurements. The resulting Pd_2Si phase is polycrystalline with randomly oriented grains. This result was found to be independent of the orientation of the Si substrate. The decomposition of the PdSi layers upon annealing at 500–700 °C is thus quite similar, whether the PdSi layer is sandwiched between two amorphous Si layers (Table I) or is laid on a Si single-crystal substrate (Table II). Polycrystalline Pd_2Si forms in either case. The excess Si precipitates out in a polycrystalline form in the first case, but grows epitaxially on the nearby single-crystalline substrate in the latter case.

Additional experiments have been performed on thermally grown PdSi. The layers were formed by vacuum deposition of Pd films, ~1000 Å thick, on Si and subsequent furnace annealing at 750 °C for ⟨100⟩-oriented substrates and 850 °C for ⟨111⟩-oriented substrates. The PdSi films produced this way were nonuniform in thickness as indicated by backscattering measurements. However, a similar transformation from PdSi to Pd_2Si was observed after annealing between 500 and 700 °C. The Pd_2Si layers possessed a laterally nonuniform structure similar to that of PdSi. Annealing of these samples at temperatures of 750–850 °C again resulted in the formation of PdSi. This $Pd_2Si \rightleftarrows PdSi$ phase transformation is thus reversible and is observed regardless of the method by which the PdSi layer is formed as long as the Pdsi layer is in contact with excess Si.

To our knowledge, the phenomenon of a reversible decomposition of a high-temperature silicide during annealing at a lower temperature has not been reported before. The observation conflicts with the equilibrium phase diagram[8] which indicates that PdSi is the stable silicide phase in contact with Si at temperatures below 850 °C. There are at least three reasons, however, why phase diagrams may not apply to thin films. Thin films are difficult to produce and anneal under exclusion of impurities. The presence of impurities may be difficult to establish, and their effects are hard to assess. We cannot exclude the possibility that impurities may affect the thermal stability of our PdSi films. We have observed the transformation regardless of the method applied to form the PdSi films, or the time and place of their preparation, and thus feel that impurities are not likely to be the cause of such a reproducible effect. A second possible cause for the effect is stress. Intrinsic and induced stresses are known to be present frequently in thin films and are sometimes high enough to fracture them. Fracturing has been observed in the case of $NiSi_2$ films grown on Si single-crystalline substrates.[10] However, a reverse transformation has not been reported in this case nor in any other silicide system in spite of the frequent presence of stress. We thus believe that the most likely cause of the effect is connected with interfacial energy because of the large surface-to-volume ratio of thin films. The importance of interfaces in thin-film reactions is well recognized, but their contribution to the equilibrium state is poorly understood mainly because interface energies are rarely known. We suggest that the present observation of a reversible decomposition of PdSi in the presence of Si is associated with the properties of that interface. It is known that thin films of Pd_2Si on a Si substrate are exceptionally stable with respect to the transformation to PdSi. A plausible reason[11] is that Pd_2Si grows nearly epitax-

TABLE II. Results of x-ray analysis of PdSi films formed by cw Ar laser scanning of a Pd|Si bilayer on Si single-crystal substrates[a] after thermal annealing between 500 and 700 °C.

Annealing conditions	Intensity of x-ray diffraction for polycrystalline PdSi	Pd_2Si	Si	PdSi	Pd_2Si	Si
	Si⟨100⟩ substrates			Si⟨111⟩ substrates		
Before annealing	Strong	Nil	Nil	Strong	Nil	Nil
500 °C, 20 min.	Medium	Medium	Nil	Strong	Nil	Nil
500 °C, 1 h.	Weak	Strong	Nil	Medium	Weak	Nil
600 °C, 1 h.	Nil	Strong	Nil	Weak	Strong	Nil
700 °C, 1 h.	Nil	Strong	Nil	Nil	Strong	Nil

[a]Two different orientations ⟨100⟩ and ⟨111⟩.

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ially on Si single-crystal substrates and especially so on the (111) surface. This produces a coherent or nearly coherent interface of low surface energy. In contrast, PdSi is not epitaxial on single-crystal substrates and the PdSi-Si interface is not coherent. Hence it is reasonable to assume that interfacial energy is high. We notice furthermore that the enthalpy change (heat of reaction) for the transformation of PdSi to Pd_2Si and Si is + 6.9 kcal/g mole using the tabulated values of 20.7 and 13.8 kcal/g mole for the heats of formation for bulk PdSi and Pd_2Si at room temperature.[12] By including the contributions of the specific heats, this enthalpy change reduces to an estimated value of approximately 0.8–1.0 kcal/g-mole at ~600 °C.[7] For a 1000-Å PdSi film this corresponds to an enthalpy change of about 20 erg/cm^2. We do not know the energies of the Si interfaces with PdSi or Pd_2Si, but values of 10^3 erg/cm^2 are quite typical of surface or interface energies for solids, so that surface energy differences could easily exceed the bulk enthalpy change in the transformation from PdSi to Pd_2Si on Si.

The rate of decomposition of PdSi depends on the structure and orientation of the Si; it is fastest on Si⟨100⟩, slower on Si⟨111⟩, and slowest on amorphous Si. This difference is consistent with the fact that the epitaxial growth rate of Si is faster on Si ⟨100⟩ than on Si⟨111⟩.[13] For amorphous Si, decomposition of PdSi did not occur until Si recrystallized as shown in Table I. Consequently, the rate is slightly slower than that for crystal Si because crystallization of Si takes place at temperatures of ~500–650 °C. Without the presence of Si, PdSi is stable in contact with Pd_2Si or SiO_2.

We believe that the reversible-phase transformation phenomenon observed for PdSi and Pd_2Si described above could exist in other silicide forming systems as well. However, it is difficult to predict the presence of such transformation. We propose that this phenomenon may exist in silicide couples which show a small difference in the heats of formation,[3] so that interface energy changes may become dominant in the thin-film reaction. The epitaxial or nonepitaxial structure of the silicides involved may then become a factor of significant influence on the interface energy or stability of the silicide-Si interface.

This structural aspect is particularly favorable in the Pd-Si system because it is the low-temperature silicide Pd_2Si that is epitaxial with respect to crystalline Si substrates, while the high-temperature silicide PdSi is nonepitaxial. No other silicide system exhibits this behavior. This may in part explain the absence of similar inverse-phase transformations in other systems. We have searched for them in the Hf-Si and Rh-Si systems but could not find any; according to Ref. 3, some phases of these systems may have closely similar bulk energies.

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